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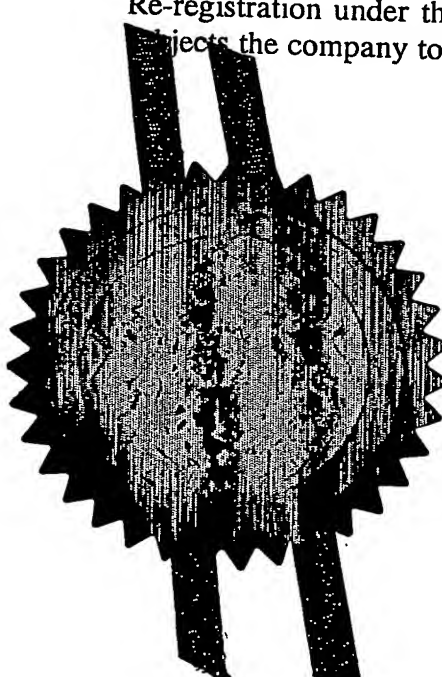
PCT

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P01/7700 0.00-0307759.1

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1. Your reference

9966

2. Patent application number
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0307759.1

3 APR 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

BP CHEMICALS LIMITED
BRITANNIC HOUSE
1 FINSBURY CIRCUS
LONDON EC2M 7BA
UNITED KINGDOM

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

4141891002

4. Title of the invention

AUTOTHERMAL CRACKING PROCESS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

HAWKINS, David George
PATENTS & AGREEMENTS
BP INTERNATIONAL LIMITED
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UNITED KINGDOM

Patents ADP number (if you know it)

7399777001

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Country

Priority application number
(if you know it)

Date of filing
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

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YES

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- b) there is an inventor who is not named as an applicant, or
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Description 10

Claim(s) -

Abstract -

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents
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11.

I/We request the grant of a patent on the basis of this application.

Signature *David Hawkins*
HAWKINS, David George

Date 3rd April 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

(01932) 763207

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AUTOTHERMAL CRACKING PROCESS

The present invention relates to the production mono-olefins by autothermal cracking of a paraffinic hydrocarbon having two or more carbon atoms especially autothermal cracking of ethane, propane, and butanes.

Olefins such as ethene and propene may be produced by a variety of processes including the steam cracking of hydrocarbons or by the dehydrogenation of paraffinic feedstocks. More recently olefins have been produced by a process known as auto-thermal cracking. In such a process a paraffinic hydrocarbon feed is mixed with an oxygen-containing gas and contacted with a catalyst which is capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising olefins. The hydrocarbon feed is partially combusted and the heat produced is used to drive the dehydrogenation reaction. Such a process is described in EP-B1-0332289.

The steam cracking of hydrocarbons to produce olefins normally co-produces other unsaturated hydrocarbons e.g. dienes. The dienes are usually separated from the steam cracker product stream which involves the use of large amounts of toxic flammable solvents e.g. acetonitrile. Once separated the dienes are considered high value products and are used in derivative processes e.g. elastomer production. However dienes are difficult to transport because they are readily degraded via oligimerisation and consequently derivative plants that employ diene feedstock are usually co-located with the sources of supply.

Wherein there is no derivative capacity to use the dienes the production of dienes becomes problematic. This is because it is not desirable that dienes be recycled

to a steam cracker due to their high propensity to cause carbonaceous fouling of the process equipment and therefore the dienes must be hydrogenated before being recycled to the steam cracker, or short furnace run-times must be tolerated, with consequent financial and operational disadvantages.

5 However it has now been found that the autothermal cracking process can be improved by co-feeding at least one unsaturated hydrocarbon, in particular a diene, with the paraffinic hydrocarbon feed and the molecular oxygen-containing gas to the autothermal cracker. It has been found that co-feeding at least one unsaturated hydrocarbon provides an increase in the olefin yield based on the amount of paraffinic
10 hydrocarbon feed converted. Furthermore it has been found that the majority of the unsaturated hydrocarbon can be converted and surprisingly no significant carbon formation occurs on the catalyst, and essentially no additional compounds e.g. benzene or toluene, associated with carbon formation on the catalyst are produced.

15 Accordingly the present invention provides a process for the production of olefins which process comprises feeding a paraffinic hydrocarbon-containing feedstock, at least one unsaturated hydrocarbon and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the presence of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising olefins.

20 The unsaturated hydrocarbon may derive from the product stream of a conventional steam cracking reactor. Alternatively the unsaturated hydrocarbon may also derive from the off gas stream of a fluid catalytic cracking reactor or may derive from the off gas streams of a delayed coker unit, a visbreaker unit or an alkylation unit. In addition the unsaturated hydrocarbon may be provided by a plastics recycling process
25 e.g. pyrolytic polymer cracking.

 The autothermal cracking reactor produces a product stream comprising unsaturated hydrocarbons. In a preferred embodiment of the invention the unsaturated hydrocarbon derives from the autothermal cracking product stream.

30 Consequently the present invention also provides a process for the production of olefins which process comprises the steps of:

 (a) feeding a paraffinic hydrocarbon-containing feedstock and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the

presence of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising olefins

(b) recovering at least a portion of the olefins produced in step (a) and

(c) recycling at least one unsaturated hydrocarbon produced in step (a) back to the autothermal cracker.

Preferably the hydrocarbon product stream produced in step (a) is separated into a first stream comprising hydrocarbons containing less than 4 carbon atoms and a second stream comprising hydrocarbons containing at least 4 carbon atoms.

Consequently a further embodiment of the invention provides a process for the production of ethene and/or propene which process comprises the steps of:

(a) feeding a paraffinic hydrocarbon-containing feedstock and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the presence of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising ethene and/or propene

(b) separating the hydrocarbon product stream produced in step (a) into a first stream comprising hydrocarbons containing less than 4 carbon atoms and a second stream comprising hydrocarbons containing at least 4 carbon atoms and at least one unsaturated hydrocarbon containing at least 4 carbon atoms

(c) recovering ethene and/or propene from the first stream and

(d) recycling at least a portion of the second stream to the autothermal cracker.

Preferably the unsaturated hydrocarbon containing at least 4 carbon atoms is recovered from the second stream and recycled to the autothermal cracker.

A single unsaturated hydrocarbon or a mixture of unsaturated hydrocarbons may be passed to the autothermal cracker

The unsaturated hydrocarbon may be any alkyne such as acetylene, propyne and/or a butyne. The unsaturated hydrocarbon may also be any alkene such as ethene, propene, butenes, pentenes, hexenes, heptenes and higher alkenes. The unsaturated hydrocarbon may also be a cycloalkene such as cyclopropene, cyclobutene, cyclopentene(s), cyclohexene(s), cycloheptenes and higher cycloalkenes.

The unsaturated hydrocarbon may be an aromatic compound. Any aromatic compound may be used, e.g. benzene, toluene, xylenes, ethylbenzene, styrene and

substituted styrenes, indene and substituted indenenes. Preferably the unsaturated compound may be benzene or toluene.

In a preferred embodiment the unsaturated hydrocarbon is a diene. The diene(s) may be selected from any suitable dienes but are preferably selected from propadiene, 1, 2 butadiene, 1,3 butadiene, 1,3 pentadiene, 1,4 pentadiene, cyclopentadiene, 1,3 hexadiene, 1,4 hexadiene, 1,5 hexadiene, 2,4 hexadiene, 1,3 cyclohexadiene and 1,4 cyclohexadiene, and substituted derivatives of the above, e.g alkyl substituted derivatives, eg methyl derivatives with more than one substitution per molecule, wherein the substituents may be the same or different. Most preferably the diene(s) are selected from 1,2 butadiene, 1,3 butadiene, 2 methyl 1,3 butadiene, 1,3 pentadiene, 1,4 pentadiene and cyclopentadiene. Advantageously the diene is 1,3 butadiene.

Wherein the unsaturated hydrocarbon contains at least 4 carbon atoms it may be any unsaturated compound as herein described above containing at least 4 carbon atoms. Preferably the unsaturated hydrocarbon containing at least 4 carbon atoms is selected from 1,2 butadiene, 1, 3 butadiene, 1,3 pentadiene, 1,4 pentadiene and cyclopentadiene and is advantageously 1, 3 butadiene.

The paraffinic hydrocarbon-containing feedstock may suitably be ethane, propane or butane. The hydrocarbon-containing feedstock may comprise other hydrocarbons and optionally other materials, for example methane, nitrogen, carbon monoxide, carbon dioxide, steam or hydrogen. The hydrocarbon-containing feedstock may contain a fraction such as naphtha, gas oil, vacuum gas oil, or mixtures thereof. Usually the hydrocarbon-containing feedstock comprises a mixture of gaseous paraffinic hydrocarbons, principally comprising ethane, resulting from the separation of methane from natural gas.

Usually the gas comprising at least one unsaturated hydrocarbon is pre-mixed with the paraffinic hydrocarbon-containing feedstock and subsequently passed to the autothermal cracker.

When the paraffinic hydrocarbon-containing feedstock is pre-mixed with the gas comprising at least one unsaturated hydrocarbon the resultant stream. Usually the unsaturated hydrocarbon has a weight percentage of between 0.01-50 wt%, preferably between 0.1-30 wt%; most preferably between 1-20wt% and advantageously between 2-15wt% based on the weight of the paraffinic hydrocarbon.

The molecular oxygen-containing gas may suitably be either oxygen or air. Preferably the molecular oxygen-containing gas is oxygen, optionally diluted with an inert gas, for example nitrogen.

5 The paraffinic hydrocarbon-containing feedstock, the gas comprising at least one unsaturated hydrocarbon and the molecular oxygen-containing gas may all be passed as separate streams to the autothermal cracker.

10 The composition of paraffinic hydrocarbon-containing feedstock /molecular oxygen-containing gas mixture is suitably from 5 to 13.5 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas for complete combustion to carbon dioxide and water. The preferred composition is from 5 to 9 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas.

Additional feed streams comprising at least one from carbon monoxide, carbon dioxide, steam and hydrogen may also be passed to the autothermal cracker.

15 Preferably an additional feed stream comprising hydrogen is passed to the autothermal cracker. Preferably the additional feed stream comprising hydrogen is premixed with the paraffinic hydrocarbon-containing feedstock and subsequently passed to the autothermal cracker.

20 The autothermal cracker may suitably be operated at a temperature greater than 500°C, for example greater than 650°C, typically greater than 750°C, and preferably greater than 800°C. The upper temperature limit may suitably be up to 1200°C, for example up to 1100°C, preferably up to 1000°C.

25 The autothermal cracker may be operated at atmospheric or elevated pressure. Pressures of 1-40 barg may be suitable, preferably a pressure of 1-5 barg e.g. 1.8 barg is employed. However a total pressure of greater than 5 barg may be used, usually a total pressure of greater than 15 barg. Advantageously the autothermal cracker is operated in a pressure range of between 15-40 barg, between 20-30 barg e.g. 25 barg.

30 Preferably, the paraffinic hydrocarbon-containing feedstock, the gas comprising at least one unsaturated hydrocarbon and the molecular oxygen-containing gas are fed to the autothermal cracker in admixture under a Gas Hourly Space Velocity (GHSV) of greater than 80,000 hr⁻¹ in order to minimise the formation of carbon monoxide and carbon dioxide. Preferably, the GHSV exceeds 200,000 hr⁻¹, especially greater than 1,000,000 hr⁻¹. For the purposes of the present invention GHSV is defined as:-vol. of

total feed at NTP/hour/(vol. of catalyst bed).

Suitably the catalyst is a supported platinum group metal. Preferably, the metal is either platinum or palladium, or a mixture thereof. Although a wide range of support materials are available, it is preferred to use alumina as the support. The support

5 material may be in the form of spheres, other granular shapes or ceramic foams.

Preferably, the foam is a monolith which is a continuous multichannel ceramic structure, frequently of a honeycomb appearance. A preferred support for the catalytically active metals is a gamma alumina. The support is loaded with a mixture of platinum and palladium by conventional methods well known to those skilled in the art.

10 Advantageously catalyst promoters may also be loaded onto the support. Suitable promoters include copper and tin.

Usually the products are quenched as they emerge from the autothermal cracker such that the temperature is reduced to less than 650°C within less than 150 milliseconds of formation.

15 Wherein the pressure of the autothermal cracker is maintained at a pressure of between 1.5-2.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 100-150 milliseconds of formation.

20 Wherein the pressure of the autothermal cracker is maintained at a pressure of between 2.0-5.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 50-100 milliseconds of formation.

Wherein the pressure of the autothermal cracker is maintained at a pressure of between 5.0-10.0 barg usually the products are quenched and the temperature reduced to less than 650°C within less than 50 milliseconds of formation.

25 Wherein the pressure of the autothermal cracker is maintained at a pressure of between 10.0-20.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 20 milliseconds of formation.

Finally wherein the pressure of the autothermal cracker is maintained at a pressure of greater than 20.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 10 milliseconds of formation.

30 This avoids further reactions taking place and maintains a high olefin selectivity.

The products may be quenched using rapid heat exchangers of the type familiar in steam cracking technology. Additionally or alternatively, a direct quench may be

employed. Suitable quenching fluids include water.

The present invention usually provides a percentage conversion of gaseous paraffinic hydrocarbon of greater than 40%, preferably greater than 50%, and most preferably greater than 60%.

5 Furthermore the present invention usually provides a selectivity towards mono-olefins of greater than 50%, preferably greater than 60%, and most preferably greater than 70%.

The invention will now be illustrated in the following examples;

Example 1

10 An auto-thermal cracking catalyst comprising platinum and copper deposited on alumina foam was placed in the autothermal cracker and the cracker was heated to 850°C.

A feed stream comprising ethane, nitrogen and hydrogen was passed to the autothermal cracker. Oxygen was then passed to the autothermal cracker to initiate the
15 reaction. The hydrogen to oxygen volume ratio was maintained at 1.9:1 (v/v).

Samples were analysed at oxygen to ethane feed ratios of 0.35, 0.44, 0.53 and 0.61 (v/v).

The nitrogen was then replaced with a feed stream comprising 9.65 volume % of 1, 3 butadiene in nitrogen and the analysis repeated.

20 The % conversion of ethane and the selectivity towards ethylene was measured and the results are shown in table 1.

Example 2

Example 1 was repeated using a hydrogen to oxygen volume ratio of 1:1 (v/v). The % conversion of ethane and the selectivity towards ethylene was measured and the
25 results are shown in table 2.

Example 3

Example 1 was repeated using a hydrogen to oxygen volume ratio of 0.5:1 (v/v). The samples were taken at oxygen to ethane feed ratios of 0.35, 0.44, and 0.53 (v/v). The % conversion of ethane and the selectivity towards ethylene was measured and the
30 results are shown in table 3.

Table1

Autothermal cracking of ethane and ethane with butadiene over a Pt-Cu catalyst with an hydrogen to oxygen volume ratio of 1.9:1 (v/v).

	ethane	ethane butadiene	ethane	ethane butadiene	ethane	ethane butadiene	ethane	ethane butadiene
total feed rate nl/min	9.03	9.02	9.19	9.18	9.18	9.17	9.16	9.11
O ₂ : C ₂ H ₆ (v/v)	0.353	0.353	0.435	0.435	0.527	0.527	0.605	0.605
H ₂ :O ₂ (v/v)	1.994	1.986	1.958	1.969	1.868	1.886	1.841	1.826
N ₂ :O ₂ (v/v)	0.543	0.490	0.492	0.433	0.446	0.387	0.426	0.375
1,3-butadiene : ethane (v/v)	---	0.020	---	0.022	---	0.024	---	0.027
ethane conversion (%)	46.00	42.87	58.74	55.88	74.76	72.19	84.65	82.40
oxygen conversion (%)	98.42	98.12	98.30	98.42	98.48	98.75	98.73	98.84
Butadiene conversion (%)	---	93.05	---	96.24	---	97.66	----	100.00
Ethene yield (g per 100g ethane feed)	36.50	35.59	44.93	44.87	53.16	54.13	55.87	57.93
Aromatics yield (g per 100g ethane feed)	0.03	0.08	0.03	0.04	0.14	0.02	0.22	0.02
Ethene selectivity (g per 100g ethane converted)	79.35	83.03	76.49	80.29	71.11	74.98	66.00	70.30

5

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Table 2:

Autothermal cracking of ethane and ethane with butadiene over a Pt-Cu catalyst with an hydrogen to oxygen volume ratio of 1:1 (v/v).

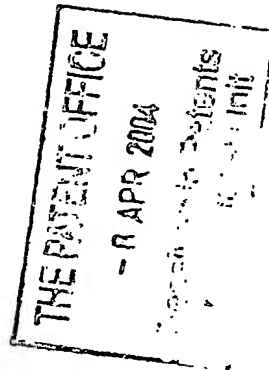
	ethane	ethane butadiene	ethane	ethane butadiene	ethane	ethane butadiene	ethane	ethane butadiene
total feed rate (nl/min)	7.62	7.62	7.77	7.76	7.76	7.74	7.71	7.66
O ₂ : C ₂ H ₆ (v/v)	0.353	0.353	0.435	0.435	0.527	0.527	0.602	0.602
H ₂ :O ₂ (v/v)	0.996	0.994	1.069	1.068	1.055	1.048	1.058	1.046
N ₂ :O ₂ (v/v)	0.538	0.484	0.483	0.433	0.443	0.400	0.431	0.378
1,3-butadiene : ethane (v/v)	---	0.021	---	0.023	---	0.026	---	0.028
ethane conversion (%)	47.86	46.15	60.97	59.14	77.10	75.43	86.44	84.98
oxygen conversion (%)	98.80	98.69	98.85	98.74	98.82	98.79	98.94	98.97
butadiene conversion (%)	---	92.86	---	92.01	---	97.47	---	98.37
Ethene yield (g/100g ethane feed)	35.59	36.14	44.10	44.98	52.13	53.58	54.35	56.33
Aromatics yield (g per 100g ethane feed)	0.03	0.03	0.02	0.05	0.03	0.13	0.10	0.13
Ethene selectivity (g per 100g ethane converted)	74.36	78.31	72.33	76.06	67.61	71.03	62.87	66.29

Table 3:

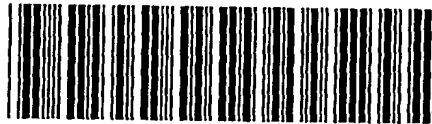
Autothermal cracking of ethane and ethane with butadiene over a Pt-Cu catalyst with an hydrogen to oxygen volume ratio of 0.5:1 (v/v).

	ethane	ethane	ethane	ethane	ethane	ethane
	butadiene		butadiene		butadiene	
total feed rate nl/min	6.95	6.95	6.76	6.74	6.62	6.58
O ₂ : C ₂ H ₆ (v/v)	0.435	0.435	0.527	0.527	0.605	0.605
H ₂ :O ₂ (v/v)	0.546	0.542	0.474	0.477	0.460	0.441
N ₂ :O ₂ (v/v)	0.488	0.442	0.452	0.399	0.425	0.378
1,3-butadiene:ethane (v/v)	---	0.024	---	0.025	---	0.030
ethane conversion (%)	64.01	63.17	78.83	79.02	88.11	87.97
oxygen conversion (%)	98.43	98.42	98.63	98.64	98.86	98.85
butadiene conversion (%)	---	98.59	---	95.49	---	93.80
Ethene yield (g per 100g ethane feed)	43.84	45.62	50.63	51.80	51.68	53.03
Aromatics yield (g per 100g ethane feed)	0.01	0.05	0.08	0.08	0.23	0.34
Ethlene selectivity (g per 100g ethane converted)	68.49	72.21	64.23	65.56	58.66	60.29

It can be seen from all the above examples that although the ethene yield is generally increased and that in all cases with the addition of butadiene the ethene selectivity is increased. Furthermore it can also be seen that the addition of the butadiene does not result in any significant carbon formation on the catalyst surface due to the fact that essentially no additional aromatics are produced.



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